Chapter 13 - Phonons

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Classical Lattice Vibrations in 3D (Harmonic approximation):

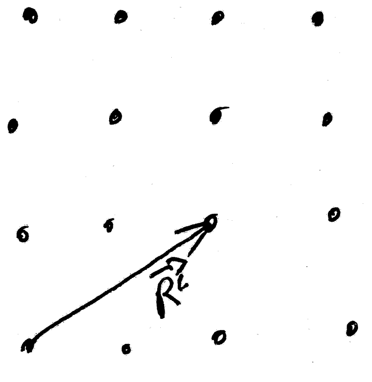
So far we have been discussing equilibrium properties of crystal lattices where we assumed that atoms (ions) are fixed to their corresponding lattice points. This is called the adiabatic approximation or Born Oppenheimer approximation. This approximation, however, was not able to explain many physical properties of crystalline solids, mainly specific heat, suggesting that there are other contributions or sources to specific heat in addition to electrons. In order to explain this, one has to assume that atoms (or ions) are still located at lattice points **R** of the Bravais lattice, but allowed to be displaced from their equilibrium sites by a small amount. Due to force acting on these atoms, they will tend to return to their equilibrium positions, resulting in lattice vibrations. Due to interactions between atoms, various atoms move simultaneously, so we have to consider the motion of the entire lattice.

We will derive the theory of the lattice vibrations by using following two assumptions:

- The ions are located on average at the Bravais lattice points **R**. For each ion, one can assign a lattice point around which the ion vibrates.

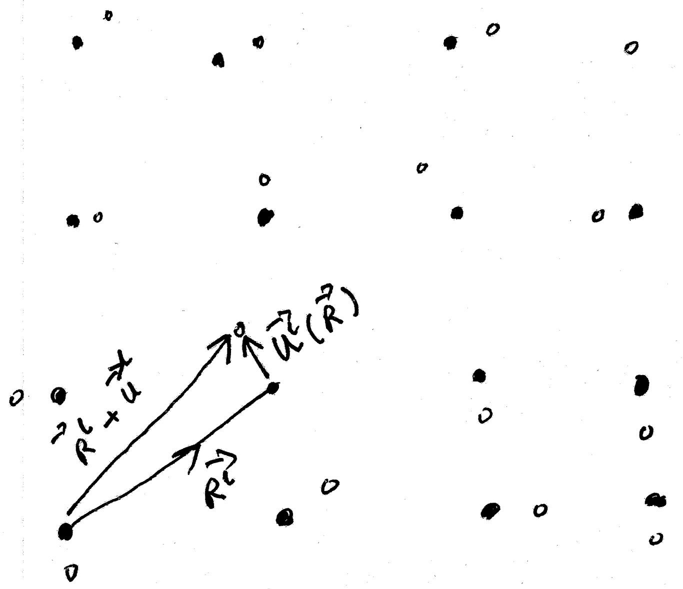
- The deviations from the equilibrium **R** are small compared with the interionic distances.

consider a crystal lattice composed of N ions located at their equilibrium positions $\vec{R}^1, \vec{R}_2^2, \ldots, \vec{R}^N$. let $\vec{u}^1, \vec{u}^2, \ldots, \vec{u}^N$ describe the vector displacement of these ions from their equilibrium positions



ideal BL lattice of ions, where ions are fixed (adiapatic approximation)

cohesive energy $\mathcal{E}_c$



$$\vec{R}^i \longrightarrow \vec{R}^i + \vec{u}^i(\vec{R})$$

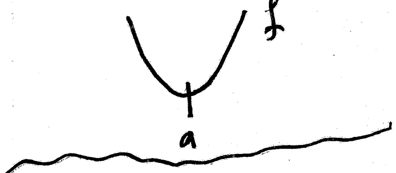
cohesiver energy $\mathcal{E} = \mathcal{E}(\vec{u}^1, \vec{u}^2, \ldots, \vec{u}^N)$

when ions move, the energy of the crystal goes up; taking the form $\mathcal{E} = \mathcal{E}(\vec{u}^1, \vec{u}^2, \ldots, \vec{u}_j^N$, where all displacements $\vec{u}^i$ are small enough such that the energy of the crystal $\mathcal{E}$ can be expanded in a Taylor series in powers of the variable u.

recall that the taylor series expansion of a function f in 1D around a minimum a, is given by

$$f(x) = f(a) + \left.\frac{\partial f}{\partial x}\right|_{x=a}(x-a) + \frac{1}{2!}\left.\frac{\partial^2 f}{\partial x^2}\right|_{x=a}(x-a)^3 + \frac{1}{3!}\left.\frac{\partial^3 f}{\partial x^3}\right|_{x=a}(x-a)^3 + \cdots$$

now for a multivariable function $f(\vec{x})$ in 3D around $\vec{a}$, where now $\vec{x}, \vec{a}$ are vectors $\vec{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_m \end{pmatrix}$; $\vec{a} = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{pmatrix}$



so if $\vec{x}$ is very close to $\vec{a}$,

then

$$f(\vec{x}) = f(\vec{a}) + \sum_{i=1}^{m} \overbrace{\left.\frac{\partial f}{\partial x_i}\right|_{\vec{x}=\vec{a}}}^{1^{st}\text{ derivative}} (x_i - a_i)$$

$$+ \frac{1}{2!}\sum_{i,j=1}^{m} \overbrace{\left.\frac{\partial^2 f}{\partial x_i \partial x_j}\right|_{\vec{x}=\vec{a}}}^{2^{nd}\text{ derivative}} (x_i - a_i)(x_j - a_j)$$

$$+ \frac{1}{3!}\sum_{i,j,k=1}^{m} \underbrace{\left.\frac{\partial^3 f}{\partial x_i \partial x_j \partial x_k}\right|_{\vec{x}=a}}_{3^{d}\text{ derivative}} (x_i - a_i)(x_j - a_j)(x_k - a_k) + \cdots$$

so the cohesive energy (total energy) $\mathcal{E}$ reads

$$\mathcal{E} = \mathcal{E}(\vec{u}^1, \vec{u}^2, \dots, \vec{u}^N) \; ; \text{ where } u^l = (u^l_x, u^l_y, u^l_z)$$

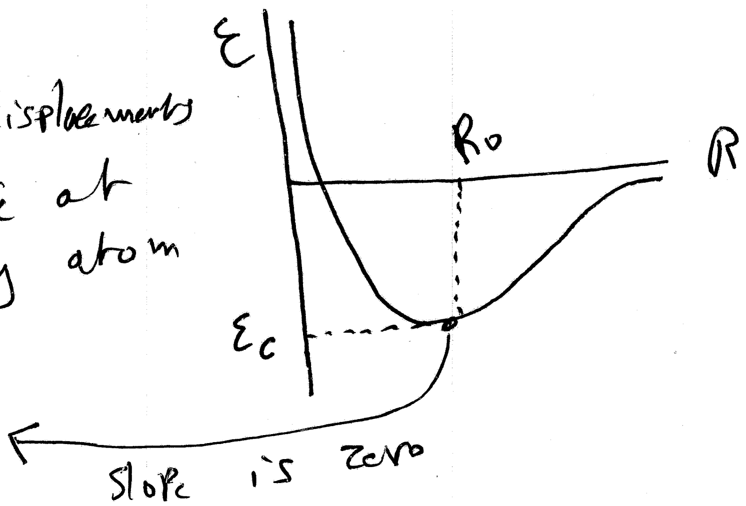
let α, β, γ be the cartesian indices, so the corrections to the cohesive energy $\mathcal{E}_c$ (when ions are fixed) is given by the Taylor series expansion of $\mathcal{E}$ in powers of u^l, so

$$\mathcal{E} = \underbrace{\mathcal{E}_c}_{\text{cohesive energy assuming ions are fixed}} + \underbrace{\frac{1}{1!}\sum_{\substack{l\\ \alpha}} \frac{\partial \mathcal{E}}{\partial u^l_\alpha}\Bigg|_{u^l_\alpha=0} u^l_\alpha}_{\text{linear term}} + \underbrace{\frac{1}{2!}\sum_{\substack{l l'\\ \alpha\beta}} \overbrace{\frac{\partial^2 \mathcal{E}}{\partial u^l_\alpha \, \partial u^l_\beta}\Bigg|_{\substack{u^l_\alpha=0\\ u^{l'}_\beta=0}}}^{\Phi^{ll'}_{\alpha\beta} \text{ force constant matrix } (3\times3)} u^l_\alpha u^{l'}_\beta}_{\text{harmonic approximation}}$$

$$\underbrace{+\frac{1}{3!}\sum_{\substack{l l' l''\\ \alpha\beta\gamma}} \frac{\partial^3 \mathcal{E}}{\partial u^l_\alpha \, \partial u^{l'}_\beta \, \partial u^{l''}_\gamma}\Bigg|_{\substack{u^l_\alpha=0\\ u^{l'}_\beta=0\\ u^{l''}_\gamma=0}} u^l_\alpha u^{l'}_\beta u^{l''}_\gamma}_{\rightarrow \text{ Anharmonic terms}} + \cdots$$

where $\alpha, \beta, \gamma = 1, 2, 3$

the linear terms in the displacements vanish as the total force at equilibrium acting on any atom is zero



$$\vec{F}_l = -\nabla \mathcal{E} = -\sum_\alpha \frac{\partial \mathcal{E}}{\partial u^l_\alpha} = 0$$

cutting the series at the second term gives the harmonic approximation. The remaining terms in the series are called Anharmonic corrections. so in the harmonic approximation, the total energy reads

$$\mathcal{E} = \mathcal{E}_c(\vec{R}^e) + \sum_{\substack{l l' \\ \alpha\beta}} \Phi^{ll'}_{\alpha\beta}\, u^{l}_{\alpha}\, u^{l'}_{\beta} \quad ---- \quad (13.13)$$

$\Phi^{ll'}_{\alpha\beta}$ is called the dynamical matrix or the force constant matrix; where it is defined as the 2nd derivative of the total energy w.r.t the lattice displacements; $\Phi^{ll'}_{\alpha\beta} = \left(\dfrac{\partial^2 \mathcal{E}}{\partial u^l_\alpha\, \partial u^{l'}_\beta}\right)_0$, where $\rightsquigarrow$ evaluated at the equilibrium positions of all ions

(properties of Φ)

① $\Phi^{ll'}_{\alpha\beta}$ is a 3X3 $\underset{\downarrow \\ \text{(real)}}{\text{symmetric}}$ matrix.

suppressing the indices α, β, symmetric matrix mean $\Phi^{ll'} = \dfrac{\partial^2 \mathcal{E}}{\partial u^l \partial u^l} = \Phi^{l'l}$

$$= \frac{\partial^2 \mathcal{E}}{\partial u^{l'} \partial u^{l}}$$

$$\begin{array}{cc} & \xrightarrow{l} \\ \downarrow l' & \begin{pmatrix} \phi^{11} & \phi^{12} & \phi^{13} \\ \phi^{21} & \phi^{22} & \phi^{23} \\ \phi^{31} & \phi^{32} & \phi^{33} \end{pmatrix} \end{array} ; \quad \begin{array}{l} \phi^{12} = \phi^{21} \\ \phi^{13} = \phi^{31} \\ \vdots \end{array}$$

(3X3) and so on

② Translational invariance (rigid translation)

$$\therefore \mathcal{E} = \underset{\hookrightarrow \text{constant}}{\mathcal{E}_c(\vec{R})} + \sum_{l}\sum_{l'} \Phi^{ll'} u^l u^{l'}$$; suppressing α, β indices

the total force acting on an ion located at $\vec{R}^l$ due to all other ions is given by

$$F_l = (-\nabla \mathcal{E})_l = -\frac{\partial \mathcal{E}}{\partial u^l} = -\sum_{l'} \Phi^{ll'} u^{l'}$$

$$\Rightarrow \boxed{M \ddot{\vec{u}}^l = -\sum_{l'} \Phi^{ll'} u^{l'}} \quad \cdots (13.15)$$

α, β are being suppressed.

equation of motion of the atom (ion) located at $\vec{R}^l$

in components form this takes the form

$$M \ddot{u}^l_\alpha = -\sum_{l'\beta} \Phi^{ll'}_{\alpha\beta} u^{l'}_\beta \quad ; \quad \alpha = 1,2,3 \quad \beta = 1,2,3$$

notice that the energy of the crystal can not change if all ions are simultaneously displaced by a single constant vector (i.e $\vec{u}^1 = \vec{u}^2 = \vec{u}^3 \cdots = \vec{u}^N = \text{constant}$).

This means that $\ddot{\vec{u}}^l = 0 \overset{\text{from (13.15)}}{\Rightarrow} \sum_{l'} \Phi^{ll'} u^{l'} = 0$

but $u^{l'} \neq 0 \Rightarrow \boxed{\sum_{l'} \Phi^{ll'} = 0} \quad \cdots (13.19)$

this implies that for rigid translation, the sum of the matrix elements of any row or any column of the matrix $\Phi^{ll'}$ vanish.

③ due to lattice translational invariance, the matrix $\Phi^{ll'}$ depends only on the distance $\vec{R}^l - \vec{R}^{l'}$; i.e

$$\Phi^{ll'} = \Phi^{ll'}(\vec{R}^l - \vec{R}^{l'})$$

Again, the equation of motion of the l^{th} atom is

$$M\ddot{\vec{u}}^{l} = -\sum_{l'} \Phi^{ll'} u^{l'} \; ; \qquad l = 1,2,\dots,N$$

Normal modes of vibrations: to find the solution of the above equation, try the plane wave solution

$$u^{l}(t) = \vec{\epsilon}\, e^{i\vec{k}\cdot\vec{R}^{l}}\, e^{-i\omega t}$$

; where $\vec{\epsilon}$ is the polarization vector $\vec{\epsilon} = \begin{pmatrix}\epsilon_1\\ \epsilon_2\\ \epsilon_3\end{pmatrix} = \begin{pmatrix}\epsilon_x\\ \epsilon_y\\ \epsilon_z\end{pmatrix}$, substitution of $u^{l}(t)$ into the equation of motion yields

$$-M\omega^2\vec{\epsilon}\, e^{i\vec{k}\cdot\vec{R}^{l}}\, \cancel{e^{-i\omega t}} = -\sum_{l'} \Phi^{ll'}(\vec{R}^{l}-\vec{R}^{l'})\, \vec{\epsilon}\, e^{i\vec{k}\cdot\vec{R}^{l'}}\, \cancel{e^{-i\omega t}}$$

$$M\omega^2 I\vec{\epsilon} = \underbrace{\sum_{l'} \Phi^{ll'} e^{i\vec{k}\cdot(\vec{R}^{l'}-\vec{R}^{l})}}_{\Phi(\vec{k})}\, \vec{\epsilon}$$

unit matrix

$$I = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

$$\Rightarrow M\omega^2 I\vec{\epsilon} = \underbrace{\Phi(\vec{k})}_{\text{eigenvalue}}\, \underset{\text{eigenvector}}{\underline{\underline{\vec{\epsilon}}}} \qquad \text{eigenvalue problem}$$

this equation represents 3 coupled equations for $\epsilon_1, \epsilon_2, \epsilon_3$, resulting in 3 different dispersion relations with 3 different frequences

$$\omega_{k\nu} = \omega_\nu(k) = \begin{Bmatrix}\omega_1(\vec{k})\\ \omega_2(\vec{k})\\ \omega_3(\vec{k})\end{Bmatrix}$$

, and 3 eigenvectors

$$\vec{\epsilon}_{k\nu} = \vec{\epsilon}_\nu(\vec{k}) \; ; \quad \vec{\epsilon}_1(\vec{k}) \; ; \; \vec{\epsilon}_2(k) \, , \; \vec{\epsilon}_3(\vec{k})$$

these 3 eigenvectors are orthonormal, so

$\vec{\epsilon}_{ki} \cdot \vec{\epsilon}_{kj} = \delta_{ij}$; for example

$\epsilon_1(k) = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$; $\epsilon_2(k) = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$, and $\epsilon_3(k) = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$

the corresponding eigenvalues are given by

$\Phi_\nu(\vec{k}) = M\omega_{k\nu}^2 \overset{\text{or}}{=} M\omega_\nu^2(k)$; i.e

$\Phi_1(\vec{k}) = M\omega_1^2(k)$; $\Phi_2(\vec{k}) = M\omega_2^2(k)$; $\Phi_3(\vec{k}) = M\omega_3^2(\vec{k})$

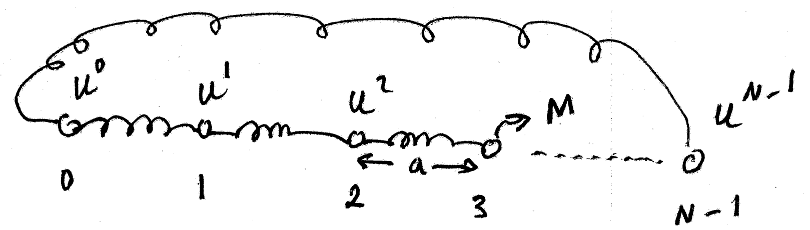
- the harmonic vibrations of an atom will produce a wave that propagates through the crystal. This wave has a wave number $\vec{k}$ (could be in any direction). This propagating wave will interact with other atoms causing each atom to vibrate with 3 possible modes (1 longitudinal and 2 transverse). i.e $\vec{\epsilon}_1 \parallel \vec{k}$ and $\vec{\epsilon}_2, \vec{\epsilon}_3 \perp \vec{k}$, so the total # of modes for a crystal of N atoms is $3N$ = (1N long + 2N Tran) notice that the source of the wave could be also due to external event like sound waves incident on crystals. in conclusion, Finding the dynamical matrix is not an easy task. However, for simple problems, one can set up directly the equations of motions and solve them easily as will be seen in the next two examples

13.2 Vibrations of a Classical Lattice

13.2.1 Classical Vibrations in One Dimension

Consider a one dimensional chain of ions of mass M sitting at equilibrium distance *a* connected by springs of constant K, as shown in figure. There are N ions, and the total length of the chain is L = N*a*. let us assume that the last atom is connected to the first atom to form a ring. This is important to satisfy the periodic boundary conditions and to make sure that the environment of each atom is equivalent to each other.

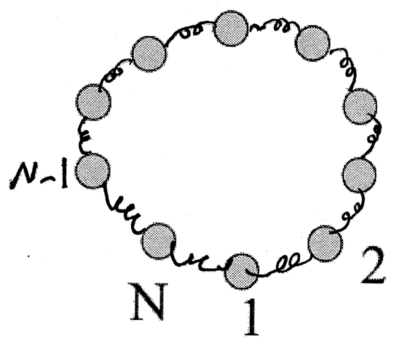
$L = Na$



<u>PBC:</u> let u^l be the deviation of the atom l with $l = 0, 1, 2, \dots, N-1$

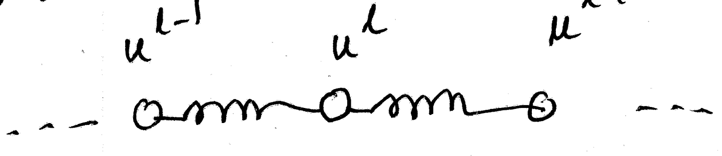
so $u^N = u^0$; or $u^{N+1} = u^1$, and <u>so on</u>

the equation of motion of the atom l is



$M\ddot{u}^l = K(u^{l+1} - u^l) + K(u^{l-1} - u^l)$; taking into account only the 1st nearest neighbor interactions

K: force constant



Try plane wave solution

$u^l = \epsilon e^{ikla} e^{-i\omega t}$; $u^{l+1} = \epsilon e^{ik(l+1)a} e^{-i\omega t}$; $u^{l-1} = \epsilon e^{ik(l-1)a} e^{-i\omega t}$

with PBC $u^N = u^0$ $\Rightarrow$

$\epsilon e^{ikNa} e^{-i\omega t} = \epsilon e^{-i\omega t} \Rightarrow e^{ikNa} = 1 \Rightarrow \cos(kNa) = 1$

$\Rightarrow kNa = 2\pi n \Rightarrow k = \frac{2\pi}{Na} n = \frac{2\pi n}{L}$; $n = 0, 1, \dots, N-1$

substituting u^l, u^{l+1}, u^{l-1} into the eq^n of motion gives

$$-M\omega^2 \epsilon e^{ikla} e^{-i\omega t} = K(e^{ika} - 1) e^{ikla} e^{-i\omega t} + K(e^{-ika} - 1) e^{ikla} e^{-i\omega t}$$

$-M\omega^2 = K(e^{ika}+e^{-ika}-2) \Rightarrow -M\omega^2 = K(2\cos(ka)-2)$

$\Rightarrow M\omega^2 = 2K(1-\cos(ka))$; using $\sin^2\theta = \frac{1}{2}(1-\cos 2\theta)$

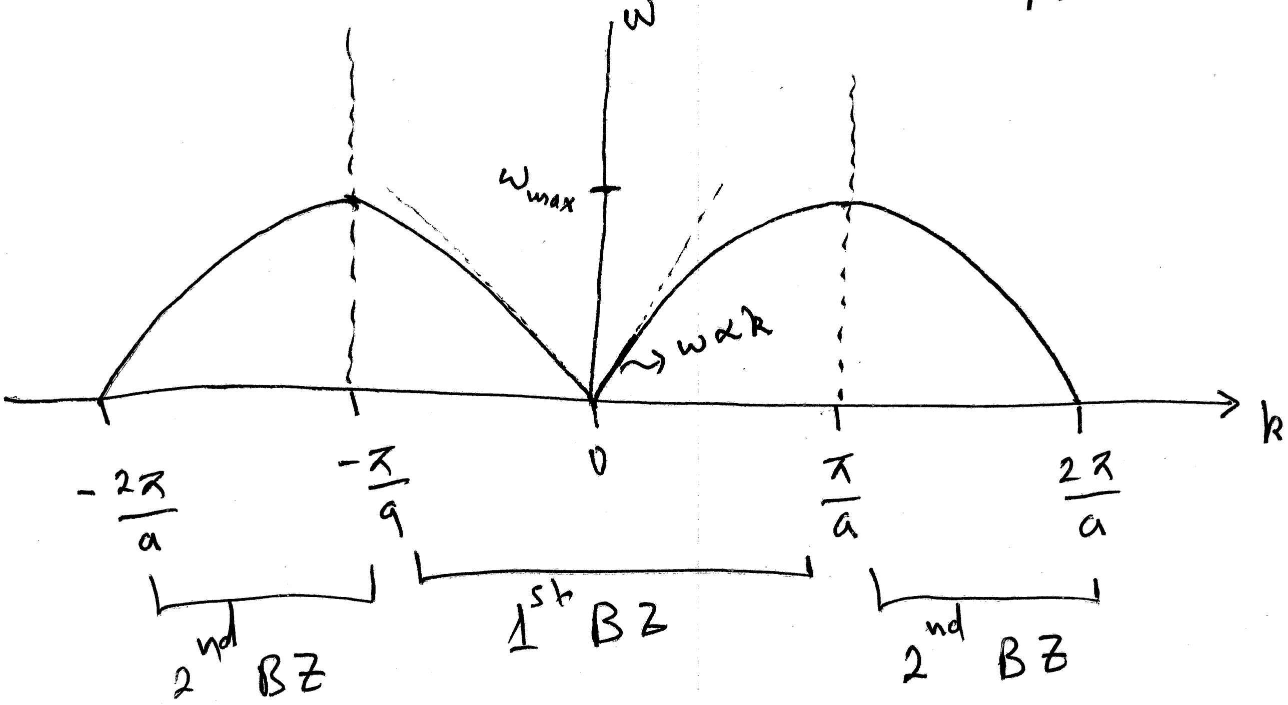
$2\sin^2\theta = 1-\cos 2\theta$

$\Rightarrow \omega^2 = \frac{2K}{M}\, 2\sin^2\left(\frac{ka}{2}\right)$

$\Rightarrow \omega(k) = 2\sqrt{\frac{K}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$; provided $K>0$

→ dispersion relation

$= \omega_{max}\left|\sin\left(\frac{ka}{2}\right)\right|$; $\omega_{max} = 2\sqrt{\frac{K}{M}}$



Remarks:

① reducing to the FBZ; the displacement of the atom l u^l and the frequency $\omega(k)$ do not change when we change k by $k+\frac{2\pi}{a}$ (or $ka \to ka+2\pi$)

$u^l = \epsilon e^{ikal} e^{-i\omega t}$; let $ka \to ka+2\pi$

$$u^l(ka+2\pi) = \epsilon e^{il(ka+2\pi)} e^{-i\omega b} = \epsilon e^{ilka} e^{-i\omega b} e^{i2\pi l}$$

$$= u^l \underbrace{e^{i2\pi l}}_{=1}$$

but $e^{i2\pi l} = 1$

as l is an integer $l = 0, 1, 2, \dots, N-1$

$$\therefore \quad u^l(ka) = u^l(ka \pm 2\pi)$$

- similarly for $\omega(k) = \omega_{max} \left| \sin\left(\frac{ka}{2}\right) \right|$

let $ka \to ka + 2\pi \Rightarrow \omega(ka+2\pi) = \omega_{max} \left| \sin\left(\frac{ka}{2} + \pi\right) \right|$

using $\sin(a+b) = \sin a \cos b + \cos a \sin b$

$$\Rightarrow \omega(ka+2\pi) = \omega_{max} \left| \sin\left(\frac{ka}{2}\right) \cos\pi + \cos\left(\frac{ka}{2}\right) \cancelto{0}{\sin\pi} \right|$$

$$= \omega_{max} \left| \sin\left(\frac{ka}{2}\right) \right|$$

This means that these solutions ($u^l(ka)$; $u^l(ka \pm 2\pi)$) are identical. This allows us to set the range of independent values of k within the FBZ i.e $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$. So any value of k outside the FBZ can be mirrored to the FBZ by an appropriate subtraction of reciprocal lattice vector

Ex! if $ka = 1.8\pi \Rightarrow ka = -0.2\pi$ in FBZ

if $ka = 4.2\pi \Rightarrow ka = 0.2\pi$ in FBZ

② Long wavelengths limit $ka \ll 1$ or $\lambda = \frac{2\pi}{k}$

$\lambda \gg a$

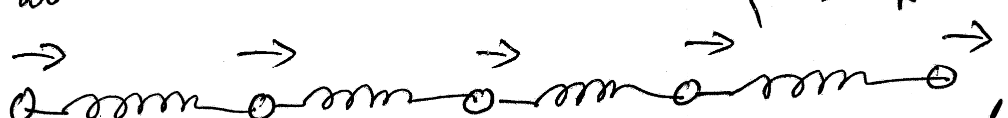
expanding $\cos ka \simeq 1 - \frac{1}{2}(ka)^2$; $\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \cdots$

$$\Rightarrow \omega^2(k) = \frac{2K}{M}\left[1 - \cos(ka)\right]$$

$$= \frac{K}{M}k^2a^2 \Rightarrow \omega = \sqrt{\frac{K}{M}}\, a\, k \Rightarrow \omega \propto k$$

linear

and $\frac{u^{l+1}}{u^l} = e^{ika} \simeq 1 \Rightarrow \underbrace{u^{l+1} = u^l \text{, indicating}}$ that all atoms move in phase $\left\{\begin{array}{l}\text{velocity of sound} \\ v_s = \frac{\omega}{k} = \sqrt{\frac{K}{M}}\, a = \text{constant} \\ \text{independent of } \underline{\underline{k}}\end{array}\right.$

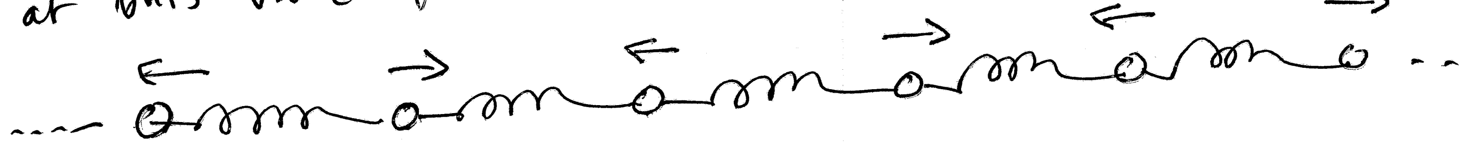


Longitudinal Acoustical mode

③ at the Zone Boundary, $ka = \pm\pi$ ($\lambda \sim a$) [short wavelength limit]

$$\frac{u^{l+1}}{u^l} = \frac{C e^{i(ka(l+1) - \omega t)}}{C e^{i(kal - \omega t)}} = e^{ika} = e^{\pm i\pi} = -1$$

$\Rightarrow u^{l+1} = -u_l$ meaning every atom is oscillating out of phase with its 2 nearest neighbors. That is, a wave at this value of k is a standing wave.

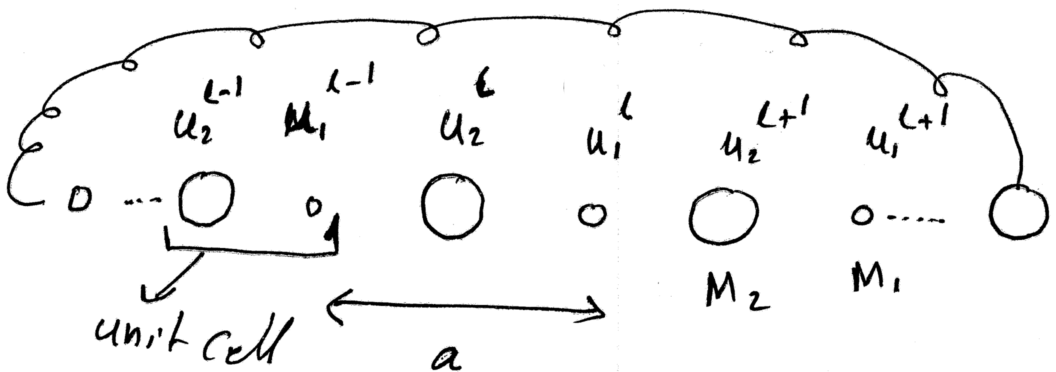


recall that in this example

# of atoms/unit cell $p = 1$; # of degrees of freedom $r = 1$

$\Rightarrow$ # of allowed modes for each atom in FBZ $= pr = 1$, so for a 1D lattice of N atoms, the total # of allowed modes (k's) in the FBZ $= N$

One-dimensional lattice with 2 atoms/unit cell:



in general and for p atoms/unit cell, we have $3p$ branches for $w(k)$ divided as follow

3 Acoustical branches and $3p-3$ optical branches

so if $p=2$, we have

3 Acous. branches (LA, 2TA) and 3 optical branches (LO, 2TO)

Acoustical branch: contains long wavelengths vibrations of the form $\omega = v_s k$; v_s : speed of sound.

Optical branch: occurs at much higher frequences (short wavelengths), so a probe at optical frequences is needed to excit these modes.

- Now Assuming again that each atom interacts only with its nearest neighbors, we have for equations of motions

$$M_1 \ddot{u}_1^l = K(u_2^{l+1} - u_1^l) + K(u_2^l - u_1^l) \quad ---- \; (1)$$

$$M_2 \ddot{u}_2^l = K(u_1^l - u_2^l) + K(u_1^{l-1} - u_2^l) \quad --- \; (2)$$

∴ $M_1 \ddot{u}_1^l = K(u_2^l - 2u_1^l + u_2^{l+1})$ ---- (1)

$M_2 \ddot{u}_2^l = K(u_1^{l-1} - 2u_2^l + u_1^l)$ --- (2)

try solutions of

$u_1^l = \epsilon_1 e^{ikla} e^{-iwt}$ and $u_2^l = \epsilon_2 e^{ikla} e^{-iwb}$

substitute back in (1) and (2)

$-M_1 w^2 u_1^l = K(u_2^l - 2u_1^l + u_2^l e^{ika})$

$\Rightarrow \boxed{(2K - M_1 w^2) u_1^l - K(1+e^{ika}) u_2^l = 0}$ --- (3)

and

$-M_2 w^2 u_2^l = K(u_1^l e^{-ika} - 2u_2^l + u_1^l)$

$\Rightarrow \boxed{-K(1+e^{-ika}) u_1^l + (2K - M_2 w^2) u_2^l = 0}$ --(4)

(3) and (4) have a solution only if the determinant of u_1^l and u_2^l vanish ⇒

$$\begin{vmatrix} (2K - M_1 w^2) & -K(1+e^{ika}) \\ -K(1+e^{-ika}) & (2K - M_2 w^2) \end{vmatrix} = 0$$

$(2K - M_1 w^2)(2K - M_2 w^2) - K^2(1+e^{ika})(1+e^{-ika}) = 0$

$4K^2 - 2K M_2 w^2 - 2K M_1 w^2 + M_1 M_2 w^4 - K^2(1 + \underbrace{e^{ika} + e^{-ika}}_{2\cos ka} + 1) = 0$

$M_1 M_2 w^4 - 2K(M_1 + M_2) w^2 + 4K^2 - K^2(2 + 2\cos ka) = 0$

" " $+4K^2 - 2K^2 - 2K^2 \cos ka = 0$

" " $+2K^2(1 - \cos ka) = 0$

$$\Rightarrow M_1 M_2 w^4 - 2K(M_1+M_2)w^2 + 4K^2 \sin^2\left(\frac{ka}{2}\right) = 0$$

$$w^2 = \frac{2K(M_1+M_2) \pm \sqrt{4K^2(M_1+M_2)^2 - 16K^2 M_1 M_2 \sin^2(ka/2)}}{2M_1M_2}$$

$$\boxed{w^2 = K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \sqrt{K^2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4K^2}{M_1M_2}\sin^2\left(\frac{ka}{2}\right)}}$$

two branches w_+^2 : optical branch

w_-^2 : Acoustical branch

Two limits:

① $ka \ll 1$; $\sin\theta \approx \theta$; $\sin^2\left(\frac{ka}{2}\right) \approx \frac{k^2a^2}{4}$

$$\Rightarrow w^2 = K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \sqrt{K^2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4K^2}{M_1M_2}\frac{k^2a^2}{4}}$$

$$= K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\sqrt{1 - \frac{k^2a^2}{M_1M_2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2}}$$

using $(1-x)^{1/2} \approx 1 - \frac{x}{2}$

$$= K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\left[1 - \frac{k^2a^2}{2M_1M_2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2}\right\}$$

$$= K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \left[K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) - \frac{k^2a^2K}{2(M_1+M_2)}\right\}$$

$$\Rightarrow w_+^2 = 2K\left(\frac{1}{M_1}+\frac{1}{M_2}\right) - \overset{\text{small}}{\cancel{\frac{k^2a^2K}{2(M_1+M_2)}}} \approx 2K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)$$

optical branch

$$\Rightarrow w_+ \approx \sqrt{2K\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}$$

and $\omega_-^2 = \frac{k^2 a^2 K}{2(M_1+M_2)} \Rightarrow \omega_- = \sqrt{\frac{K}{2(M_1+M_2)}}\; a\, k$

acoustical branch

Atoms movements

ω_+ : substitute ω_+^2 in (3)

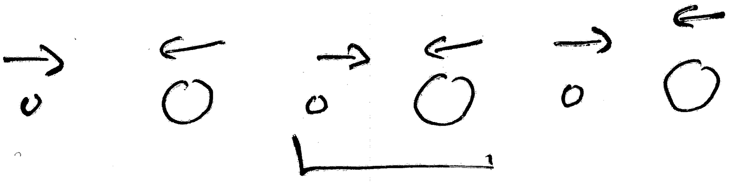
$(2K - M_1\omega_+^2)u_1^l - K(1+e^{ika})u_2^l = 0$; $e^{ika} \approx 1$

$2Ku_1^l - 2K(1+\frac{M_1}{M_2})u_1^l - K[1+1]u_2^l = 0$

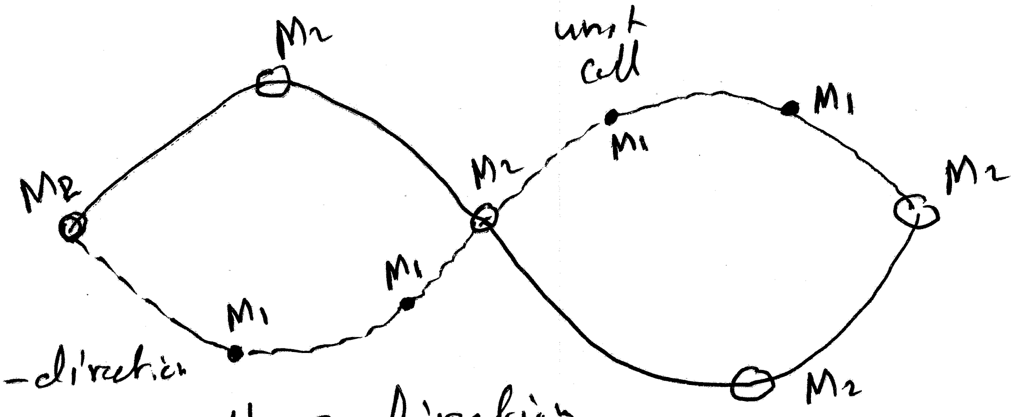
$2K[1-1-\frac{M_1}{M_2}]u_1^l = 2Ku_2^l \Rightarrow -\frac{M_1}{M_2}u_1^l = u_2^l$

$\Rightarrow \frac{u_1^l}{u_2^l} = -\frac{M_2}{M_1}$ atoms within unit cell vibrate out of phase

LO(1)



TO(2)



one in y-direction
and another on in the z direction
assuming wave propagate in x-direction

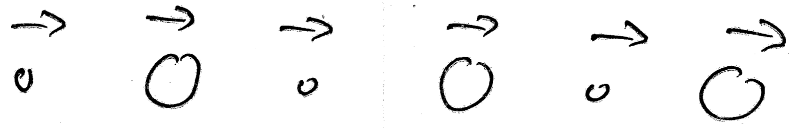
ω_- : substitute ω_-^2 in (3), we get

$(2K - M_1\omega_-^2)u_1^l - K(1+e^{-ika})u_2^l = 0$; $e^{-ika} \approx 1$

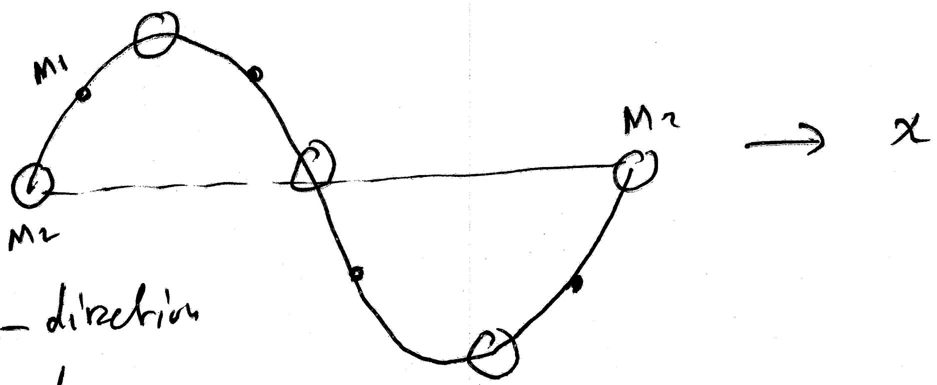
$\left(2K - M_1 \underbrace{\cancel{\frac{k^2a^2K}{2(M_1+M_2)}}}_{\text{small}}\right)u_1^l - 2Ku_2^l = 0 \Rightarrow u_1^l = u_2^l$

atoms within unit cell vibrate in phase

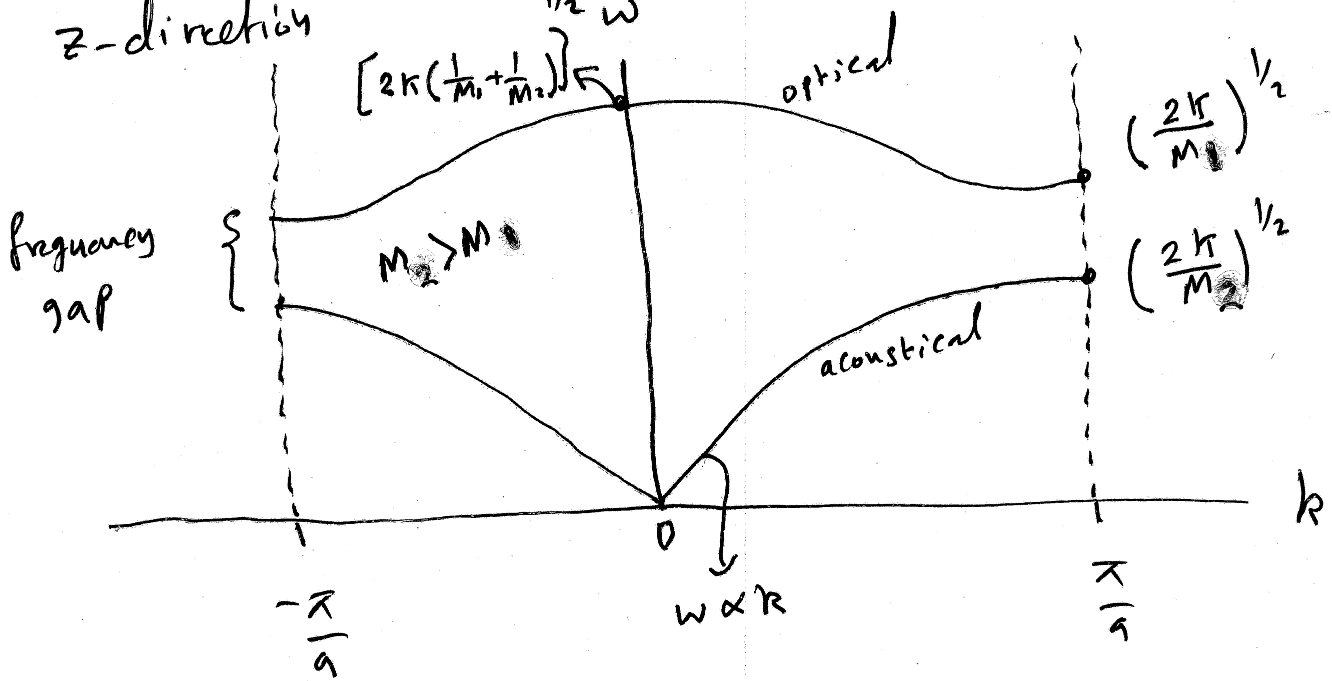
LA(1)



TA(2)



one along y-direction and the other is along z-direction



② at $k_{max} = \pm \pi/2 \Rightarrow \sin\left(\frac{ka}{2}\right) = 1$

$$\omega^2 = \frac{2K(M_1+M_2) \pm \sqrt{4K^2(M_1+M_2)^2 - 16K^2M_1M_2\sin^2\left(\frac{ka}{2}\right)}}{2M_1M_2}$$

$$= \frac{2K(M_1+M_2) \pm \sqrt{4K^2M_1^2 + 4K^2M_2^2 + 8K^2M_1M_2 - 16K^2M_1M_2}}{2M_1M_2}$$

$$w^2 = \frac{2K(M_1+M_2) \pm \sqrt{4K^2(M_1^2+M_2^2-2M_1M_2)}}{2M_1M_2}$$

$$= \frac{2K(M_1+M_2) \pm \sqrt{4K^2(M_2-M_1)^2}}{2M_1M_2}$$; assuming $M_2 > M_1$

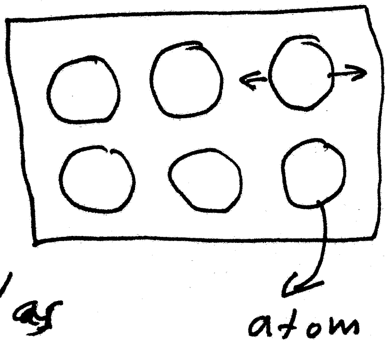
$$= \frac{2K(M_1+M_2) \pm 2K(M_2-M_1)}{2M_1M_2}$$

$$\Rightarrow w_+^2 = \frac{2\cancel{KM_1}+2KM_2+2KM_2-2\cancel{KM_1}}{2M_1M_2} = \frac{2K}{M_1}$$

$$w_-^2 = \frac{2KM_1+2KM_2-2KM_2+2KM_1}{2M_1M_2} = \frac{2K}{M_2}$$

QM Lattice vibrations

consider a solid consisting of N atoms. The atoms vibrate contineously about their equilibrium positions. classically these vibrations are called normal modes. for a solid of N atoms, there are 3N normal modes divided as (1N longitudinal modes + 2N transverse modes). each mode of vibration propagate through the solid with a speed of sound.



Quantum mechanically, each mode of vibration is quantized and called a phonon. a phonon is a massless excitation with zero spin and has an energy-momentum relation $\varepsilon = cp$; c: propagation speed

and has dispersion relation of $\omega = ck$

so in solid of N atoms, there are 3N phonons. These phonons form an ideal Bose gas (i.e ensemble of bosons) that can be described by Bose-Einstien statistics. Now each phonon is usually represented by 1D harmonic oscillator, so there are 3N independent harmonic oscillators in a solid of N atoms. $\Rightarrow \varepsilon = cp = c\hbar k = c\hbar \frac{\omega}{c} = \hbar\omega$

Now eah phonon is represented by a 1D H.O with energy

$\varepsilon = (n+1/2)\hbar\omega$; ignoring the zero point energy

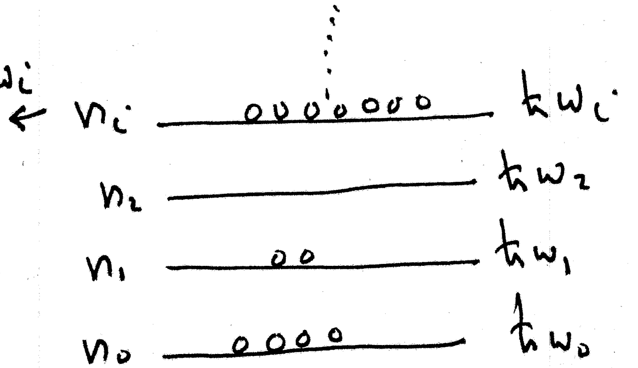
$\Rightarrow \varepsilon = n\hbar\omega$; $n = 0, 1, 2, 3, ----$

So for a solid of N atoms, there are 3N harmonic oscillators with characterstic frequencies $\omega_0, \omega_1, \omega_2, ---$ and a characterstic corresponding energies $\hbar\omega_0, \hbar\omega_1, ---$

So these phonons are to be distributed among differen energy levels, where each level has a specific frequency ω_i, energy $\hbar\omega_i$, and an average occupation # of n_i given by

$$\langle n_i \rangle = \frac{1}{e^{\beta\hbar\omega_i} - 1}$$

;

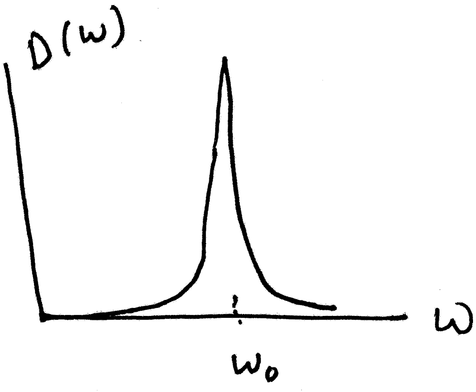


again with $\mu = 0$, as the # of phonons in a solid is not conserved. each single particle state can be occupie by any # of phonons, as Pauli principle is not applied to a system of Bosons.

Now there are two models for studying phonons in a solid; Ginstien model and Debye model.

① Einstien model:

Assumed that all phonons in a solid have the same frequency; i.e all harmonic oscillators have a common frequency ω_0 with the density of states is given by $D(\omega) = 3N\,\delta(\omega-\omega_0)$



- in principle, there are N atoms in a solid. Thus we should have N H.Os. but for each oscillator there are 3 Polarization states (1 longitudinal + 2 transverse), so overall there are 3N independent 1D H.Os, with energy given by

$$\varepsilon = \int_0^\infty \langle n(\omega)\rangle\, \hbar\omega_0\, D(\omega)\, d\omega \;;\; \langle n(\omega)\rangle = \frac{1}{e^{\beta\hbar\omega_0}-1}$$

$$= \int_0^\infty \frac{\hbar\omega_0}{e^{\beta\hbar\omega_0}-1}\, 3N\,\delta(\omega-\omega_0)\,d\omega$$

$$= \frac{\hbar\omega_0\, 3N}{e^{\beta\hbar\omega_0}} \underbrace{\int_0^\infty d\omega\, \delta(\omega-\omega_0)}_{1} = \frac{3N\,\hbar\omega_0}{e^{\beta\hbar\omega_0}-1}$$

the specific heat C_V is

$$C_V = \left(\frac{\partial \varepsilon}{\partial T}\right)_V = \frac{3N\hbar\omega_0\, e^{\frac{\hbar\omega_0}{k_BT}}\left(\frac{\hbar\omega_0}{k_BT^2}\right)}{\left(e^{\frac{\hbar\omega_0}{k_BT}}-1\right)^2}$$

$$C_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\frac{\hbar\omega_0}{k_BT}}}{\left(e^{\frac{\hbar\omega_0}{k_BT}}-1\right)^2}$$

- high T limit
  $(k_BT \gg \hbar\omega_0)$

$$C_V \approx 3Nk_B \cancel{\left(\frac{\hbar\omega_0}{k_BT}\right)^2} \frac{e^{\frac{\hbar\omega_0}{k_BT}}}{\left(1+\cancel{\frac{\hbar\omega_0}{k_BT}}-1\right)^2} \quad ; \quad e^x \approx 1+x$$

$$\approx 3Nk_B \underbrace{e^{\frac{\hbar\omega_0}{k_BT}}}_{\approx 1} \approx 3Nk_B$$ as expected for classical particles (ideal gas).

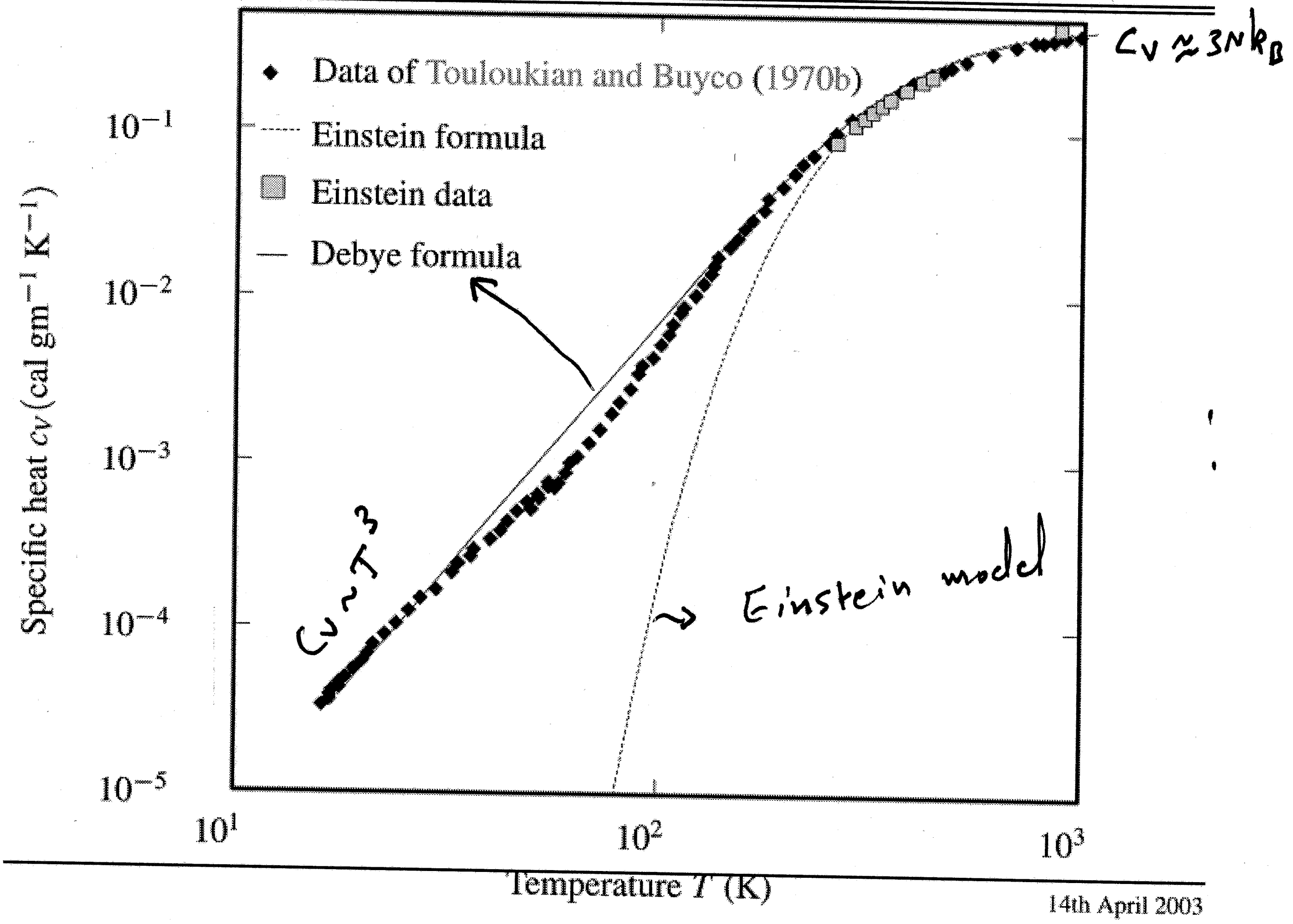
- low T limit $(k_BT \ll \hbar\omega_0)$

$$\left(e^{\frac{\hbar\omega_0}{k_BT}}-1\right)^2 \rightarrow \left(e^{\frac{\hbar\omega_0}{k_BT}}\right)^2,$$ so

$$C_V \approx 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\frac{\hbar\omega_0}{kT}}}{e^{2\frac{\hbar\omega_0}{kT}}} \approx 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 e^{-\frac{\hbar\omega_0}{k_BT}}$$

This result, however, does not fit the observed data which was observed to scale with T^3 $(C_V \sim T^3)$, so Einstein model works at high T, but fails at very low T. This is obvious from the next figure for diamond.

Phonon Specific Heat



$$\therefore\ C_V = 3Nk_B\left(\frac{\hbar\omega_0}{k_BT}\right)^2 \frac{e^{\frac{\hbar\omega_0}{k_BT}}}{\left(e^{\frac{\hbar\omega_0}{k_BT}}-1\right)^2}\ ;$$

let $T_E = \frac{\hbar\omega_0}{k_B}$ be Einstein temperature $\Rightarrow$

$$C_V = 3Nk_B\left(\frac{T_E}{T}\right)^2 \frac{e^{\frac{T_E}{T}}}{\left(e^{\frac{T_E}{T}}-1\right)^2}\ ;$$ to plot

$\frac{C_V}{3Nk_B}$ vs T, set T_E to any temperature, say, 200K

② Debye model:

Debye improved the previous model of Einstein by allowing a continuous spectrum of frequencies. First, let us find the density of single-particle states of these phonons.

$$D(\omega) = \sum_{\vec{k}\nu} \delta(\omega - \omega_{\vec{k}\nu}) = \frac{1}{(2\pi)^d} \int d\Gamma \sum_{\nu} \delta(\omega - \omega_{k\nu})$$

integral over phase space $d\Gamma = d^3q\, d^3k$

but $\nu = 3$ as there are 3 states of polarizations for phonon, so in 3D ($d=3$), we get

$$D(\omega) = \frac{1 \cdot 3}{(2\pi)^3} \underbrace{\int d^3q}_{V} \int d^3k\, \delta(\omega - \omega_k) \quad ; \quad \omega_k = \underset{\substack{\downarrow \\ \text{speed of sound in solid}}}{c}\, k$$

$$= \frac{3V}{(2\pi)^3} \int_0^\infty 4\pi k^2 dk\, \delta(\omega - \omega_k)$$

$d\omega_k = c\, dk$

$$= \frac{3V}{8\pi^3} 4\pi \frac{1}{c^3} \int_0^\infty d\omega_k\, \omega_k^2\, \delta(\omega - \omega_k)$$

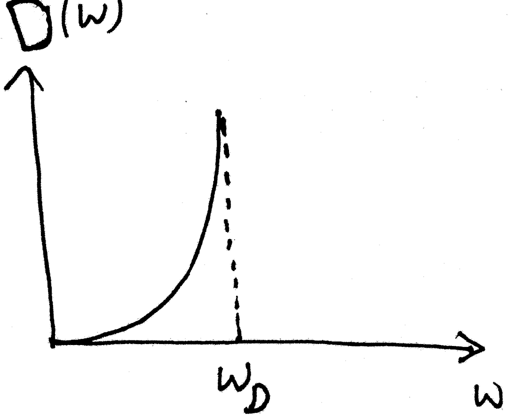
where we assumed that all 3 modes have the same speed c in the solid,

so

$$D(\omega) = \frac{3V}{2\pi^2 c^3} \int_0^\infty d\omega_k \, \omega_k^2 \, \delta(\omega - \omega_k) = \frac{3V}{2\pi^2 c^3} \omega^2$$

furthermore, Debye assumed that there is a cutoff frequency, ω_D, above which no short wavelength phonons are excited, i.e

$$D(\omega) = \begin{cases} \frac{3V}{2\pi^2 c^3} \omega^2 & , \omega < \omega_D \\ 0 & , \omega > \omega_D \end{cases}$$

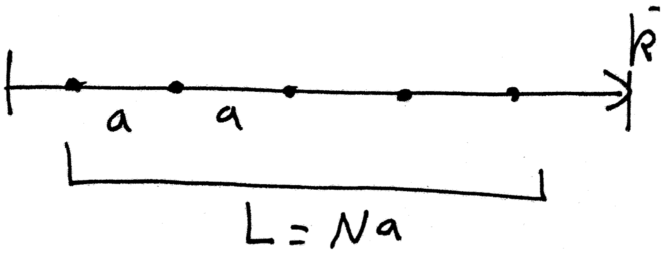


what does this mean??!

The maximum # of phonons in a solid of N atoms is fixed to the # of lattice sites (3N). This when we count every possible frequency, and every possible direction of vibration for each frequency. This limitation comes from periodic boundary conditions imposed by quantum mechanics. in general and at a temperature T, the # of phonons in a solid could be less than (3N).

Recall that a sound wave propagating in a solid can be represented by a standing wave fixed by the boundaries of the solid.

to understand why there must be an upper cut off frequency, consider a 1D lattice with separation of a. Now for a sound wave propagating through this bounded 1D crystal, the wave is a standing wave with an allowed values of $\vec{k}$ given by



$$k = \frac{\pi}{L} n$$

$n = 1, 2, ---, N$

total # of modes (phonons) = total # of allowed k's = N

so $n_{min} = 1 \Rightarrow k_{min} = \frac{\pi}{L} \equiv \frac{2\pi}{\lambda_{max}}$

$$\Rightarrow \boxed{\lambda_{max} = 2L}$$

for $n_{max} = N \Rightarrow k_{max} = \frac{\pi}{L} N = \frac{\pi N}{Na} = \frac{2\pi}{\lambda_{min}}$

$$\Rightarrow \boxed{\lambda_{min} = 2a}$$

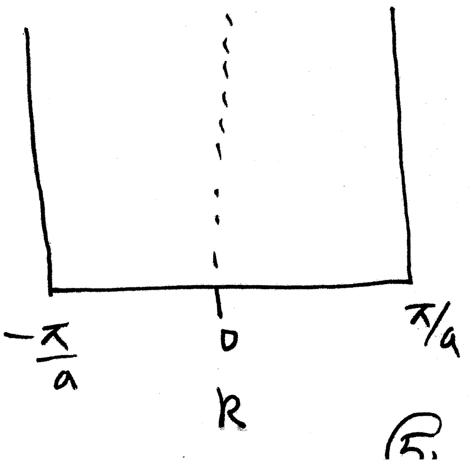
this is the minimum allowed wave length that corresponds to a maximum frequency ω_D

- Note that

$$k_{min} = \frac{\pi}{L} = \frac{\pi}{Na} \xrightarrow{N \to \infty} 0$$

and $k_{max} = \frac{\pi}{L} N = \frac{\pi \cancel{N}}{\cancel{N} a} = \frac{\pi}{a}$

these two limits define what is called the first Brillion zone



as a result, the total # of phonons in a solid of N atoms must be equal to 3N, so

$$\int_0^\infty D(\omega)\,d\omega = 3N \Rightarrow \int_0^{\omega_D} \frac{3V}{2\pi^2 c^3}\,\omega^2 d\omega = 3N$$

$$\Rightarrow \frac{3V}{2\pi^2 c^3}\,\frac{\omega_D^3}{3} = 3N \Rightarrow \omega_D^3 = 6\pi^2 c^3 \frac{N}{V} = 6\pi^2 c^3 n$$

$n = \frac{N}{V}$ = phonon density

i.e $\omega_D = (6\pi^2 n)^{1/3} c$

Now Debye temperature T_D is defined as

$$k_B T_D = \hbar\omega_D \Rightarrow T_D = \frac{\hbar\omega_D}{k_B}$$

Now the # of phonons in the frequency range $\omega \to \omega + d\omega$ is $n(\omega)d\omega = \langle n(\omega)\rangle D(\omega)\,d\omega$; when $\langle n(\omega)\rangle = \frac{1}{e^{\beta\hbar\omega}-1}$

since the energy of each phonon is $\hbar\omega$, the energy of the phonons $d\mathcal{E}$ in the frequency range $\omega \to \omega + d\omega$ is

$$d\mathcal{E} = \hbar\omega\,\langle n(\omega)\rangle D(\omega)\,d\omega$$

$$\mathcal{E}(T) = \int_0^{\omega_D} \hbar\omega \frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\,\frac{3V}{2\pi^2 c^3}\,\omega^2 d\omega = \frac{3V\hbar}{2\pi^2 c^3}\int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1}$$

let $x = \frac{\hbar\omega}{k_B T} \Rightarrow \omega = \frac{k_B T}{\hbar}x$; $d\omega = \frac{k_B T}{\hbar}dx$; $\omega = 0 \Rightarrow x = 0$; $\omega = \omega_D \Rightarrow x = \frac{\hbar\omega_D}{k_B T} = T_D/T$

so $$\mathcal{E}(T) = \frac{3V\hbar}{2\pi^2 c^3}\int_0^{T_D/T} \frac{\left(\frac{k_BT}{\hbar}\right)^4 x^3\,dx}{e^x-1} = \frac{3V\hbar}{2\pi^2 c^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{T_D/T}\frac{x^3\,dx}{e^x-1}$$

$$= \frac{3\hbar}{\frac{3}{3}\times\frac{2\pi^2c^3}{V}\times\frac{N}{N}}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{T_D/T}\frac{x^3\,dx}{e^x-1}$$

$$= \frac{9N\hbar}{\frac{6\pi^2c^3N}{V}}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{T_D/T}\frac{x^3\,dx}{e^x-1}$$

$$\boxed{\mathcal{E}(T) = \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{T_D/T}\frac{x^3\,dx}{e^x-1}}$$

Two limits

(i) high T limit ($k_BT \gg \hbar\omega$) ; $e^x \approx 1+x$

$$e^{\frac{\hbar\omega}{kT}} \approx 1+\frac{\hbar\omega}{k_BT}$$

$$\mathcal{E}(T) = \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{T_D/T}\frac{x^3\,dx}{1+x-1}$$

$$= \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4\frac{1}{3}\left(\frac{T_D}{T}\right)^3 = 3Nk_BT$$; when I used $\omega_D = \frac{k_BT_D}{\hbar}$

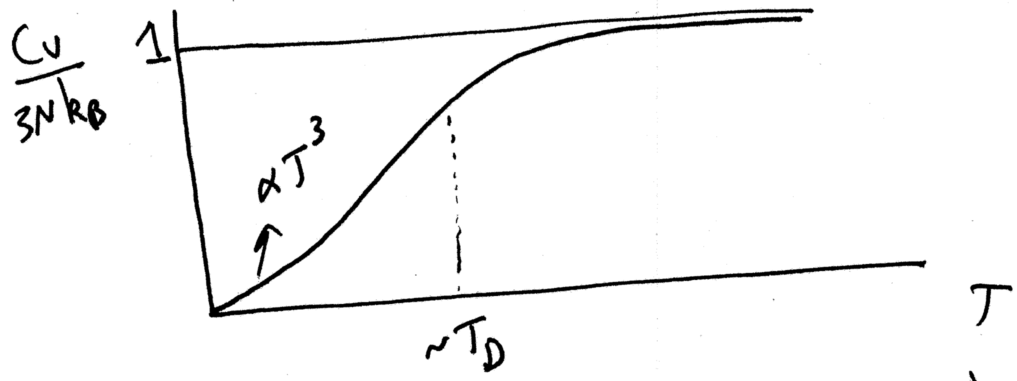
$\Rightarrow C_V = \left(\frac{\partial\mathcal{E}}{\partial T}\right)_V = 3Nk_B$ as expected

(ii) low T limit ($k_BT \ll \hbar\omega$) ; $\frac{T_D}{T} \to \infty$

$$\mathcal{E}(T) = \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{x^3\,dx}{e^x-1}}_{\pi^4/15}$$

$$= \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4 \frac{\pi^4}{15} = \frac{9Nk_B\pi^4}{15}\,\frac{T^4}{T_D^3}$$

so $C_v = \left(\frac{\partial \mathcal{E}}{\partial T}\right)_V \simeq 234\, N k_B \left(\frac{T}{T_D}\right)^3$ i.e $C_v \propto T^3$ in agreement with observed data



T_D of some materials

Na	150 K
Al	394 K
diamond	1860 K

Result: Debye model is successfull to describe physical properties at both high and low Temperatures

To find exact expression for C_V, we start from

$$\varepsilon = \frac{3V\hbar}{2\pi c^3}\int_0^{\omega_D}\frac{\omega^3\,d\omega}{e^{\hbar\omega/k_BT}-1} \Rightarrow C_V = \left(\frac{\partial\varepsilon}{\partial T}\right)_V$$

$$C_V = \frac{3V\hbar}{2\pi^2c^3}\frac{\partial}{\partial T}\int_0^{\omega_D}\frac{\omega^3\,d\omega}{e^{\hbar\omega/k_BT}-1} = \frac{3V\hbar}{2\pi^2c^3}\int_0 \frac{d\omega\,\omega^3\left(-e^{\frac{\hbar\omega}{k_BT}}\cdot\left(-\frac{\hbar\omega}{k_BT^2}\right)\right)}{\left(e^{\hbar\omega/k_BT}-1\right)^2}$$

$$= \frac{3V\hbar}{2\pi^2c^3}\frac{\hbar}{k_BT^2}\int_0^{\omega_D}\frac{\omega^4\,e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \;;$$

let $x = \dfrac{\hbar\omega}{k_BT} \Rightarrow \omega = \dfrac{k_BT}{\hbar}x \Rightarrow$ $\omega = 0 \Rightarrow x = 0$; $\omega = \omega_D \Rightarrow x = \dfrac{\hbar\omega_D}{k_BT} = \dfrac{T_D}{T}$

$$\Rightarrow C_V = \frac{3V\hbar^2}{2\pi^2c^3}\frac{1}{k_BT^2}\left(\frac{k_BT}{\hbar}\right)^5\int_0^{T_D/T}\frac{x^4e^x\,dx}{(e^x-1)^2}$$

$\{T_D$: Debye temperature

Now using $T_D = \dfrac{\hbar\omega_D}{k_B} \Rightarrow T_D^3 = \dfrac{\hbar^3\omega_D^3}{k_B^3} = \dfrac{\hbar^3}{k_B^3}\;\dfrac{6\pi^2c^3N}{V}$

$$\Rightarrow \pi^2c^3\hbar^3 = \frac{Vk_B^3T_D^3}{6N}$$

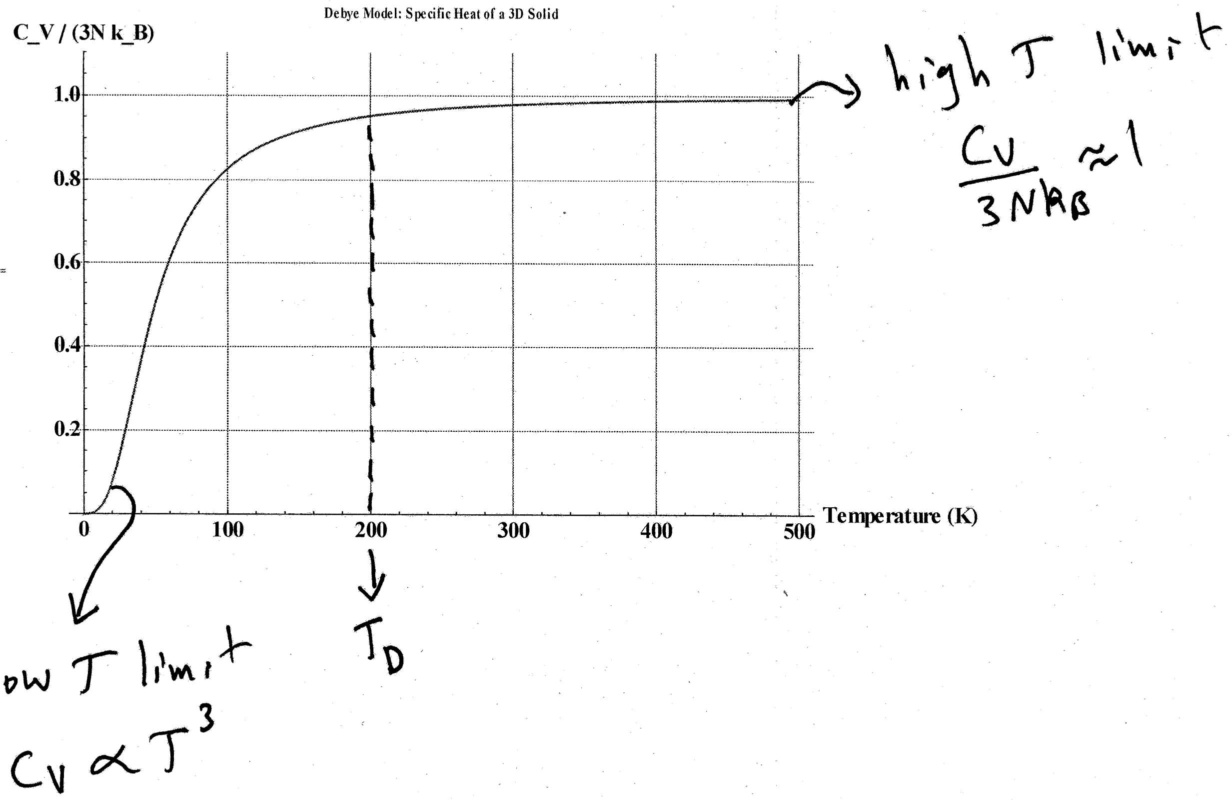
$$\Rightarrow C_V = \frac{3Vk_B^4}{2\pi^2c^3\hbar^3}T^3\int_0^{T_D/T}\frac{x^4e^x\,dx}{(e^x-1)^2} = \frac{3Vk_B^4}{2}\cdot\frac{6N}{Vk_B^3T_D^3}T^3\int_0^{T_D/T}\frac{x^4e^x\,dx}{(e^x-1)^2}$$

$$C_V = 9Nk_B\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^4e^x\,dx}{(e^x-1)^2} \Rightarrow \frac{C_V}{3Nk_B} = 3\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^4e^x\,dx}{(e^x-1)^2}$$

```
In[87]:= (*Define the dimensionless specific heat function for the Debye model in 3D*)
   CvOver3NkB[TD_, T_] := 3 * (T / TD) ^3 * NIntegrate[(x^4 * Exp[x]) / (Exp[x] - 1) ^2, {x, 0, TD / T}]

   (*Set the Debye temperature (adjust as needed)*)
   TD = 200; (*Example:Debye temperature in Kelvin*)
   (*Plot the specific heat for a wider temperature range to see the high-T limit*)
   Plot[CvOver3NkB[TD, T], {T, 0.1, 500}, (*Extended temperature range to T>>Θ_D*)
    PlotRange → {0, 1.1}, AxesLabel → {"Temperature (K)", "C_V / (3N k_B)"},
    PlotLabel → "Debye Model: Specific Heat of a 3D Solid",
    LabelStyle → Directive[Black, Bold, 20], PlotStyle → Thick, GridLines → Automatic]
```

Out[88]=



high T limit

$\frac{C_V}{3Nk_B} \approx 1$

low T limit

$C_V \propto T^3$

T_D

Total specific heat of metals

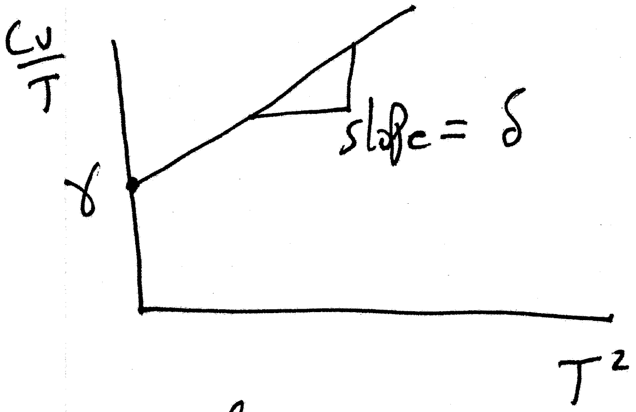
There are two contribution to specific heat in metals, electrons and phonons.

$$C_{ele} = \frac{\pi^2}{2} N k_B \frac{T}{T_F} \quad \text{and} \quad C_{ph} \approx 234 N k_B \left(\frac{T}{T_D}\right)^3$$

$$C_v = C_{ele} + C_{ph} = \underbrace{\frac{\pi^2}{2}\frac{N k_B}{T_F}}_{\gamma} T + \underbrace{\frac{234 N k_B}{T_D^3}}_{\delta} T^3$$

$$C_v = \gamma T + \delta T^3$$

i.e $$\boxed{\frac{C_v}{T} = \gamma + \delta T^2}$$



at very low T (say < 1K)

$C_{ele} >> C_{ph}$ as phonons are frozen

Note that $\gamma = \frac{\pi^2}{2}\frac{N k_B}{T_F}$ and $\delta = \frac{234 N k_B}{T_D^3}$

so once γ and δ are found experimentally, one can calculate or estimate the values of T_F and T_D